

Synthesis and Properties of Poly(*p*-phenylene terephthalamide) Bearing Both Polar and Unsaturated Substituents Introduced via Claisen Rearrangement Reaction

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ABSTRACT: A series of novel wholly aromatic copolyamides, poly(*p*-phenylene terephthalamide)-*ran*-poly[*p*-phenylene 2,5-bis(allyloxy)terephthalamide] (APPTA-*x*, *x* (=0, 5, 25, 50, 60, 75, 90, and 100) represents the molar fraction of allyloxy containing structure unit), were prepared via low temperature solution copolycondensation of *p*-phenylenediamine, terephthaloyl chloride, and 2,5-bis(allyloxy)terephthaloyl chloride. They were converted to the target copolymers, poly(*p*-phenylene terephthalamide)-*ran*-poly[*p*-phenylene 2,5-diallyl-3,6-dihydroxyterephthalamide] (CRPPTA-*x*), through Claisen rearrangement reaction, as characterized by a comprehensive analyses of NMR, FT-IR, gel permeation chromatography, and differential scanning calorimetry. Although APPTA-*x* had a poor solubility in common organic solvents, the rearranged products with high co-unit contents, that is, CRPPTA-60, 75, 90, and 100,

were readily dissolved in *m*-cresol, DMF, DMAc, DMSO, and NMP. The effect of these four polymers, used as sizing agents, on the interfacial adhesion between Kevlar fiber and epoxy resin was investigated by the contact angle method, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and microbond tests. Compared with the naked fibers, the sized fibers displayed enhanced surface energy and roughness. The fibers sized with 0.5 wt % CRPPTA-60 solution in NMP exhibited a maximum increase of 19% in interfacial shear strength. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 00, 000–000

KEYWORDS: adhesion; aramid fiber; claisen rearrangement reaction; composites; epoxy; polyamides; PPTA; sizing agent

INTRODUCTION Poly(*p*-phenylene terephthalamide) (PPTA) is one of the most important wholly aromatic polyamides. Because of the rigidity, symmetry, and intermolecular H-bonding of polymer chains, PPTA can be spun into highly oriented fibers with excellent thermal stability, high chemical resistance, low flammability and exceptional tensile strength and modulus from liquid-crystalline solution in concentrated sulfuric acid.^{1,2} The representative product, that is, Kevlar, has been comprehensively studied and widely applied in many fields such as military, aeronautics, astronautics, and automobiles.^{3–6} Kevlar and other aramid fibers have been frequently employed as reinforcing materials to fabricate high performance rubber and epoxy-based composites. However, the inferior interfacial affinity toward matrices due to the smooth surfaces and chemical inertness of fibers hinders

the full achievement of their potential. To overcome this disadvantage, the treatment of Kevlar fiber with chemical,^{7–16} plasma,^{17–19} and ultrasound²⁰ methods as well as gamma-irradiation²¹ have been developed to increase surface polarity. Most of these methods could introduce reactive sites on the fiber surface and facilitate further modification, such as grafting, but tolerate severe operation conditions and damages to the fibers. Coating the reinforcing fibers with sizing agents is an alternating way to improve interface structure.^{22–27} de Lange and coworkers developed an “adhesion activation” method by coating an epoxy-amine finish (diglycidyl ether of glycerol as epoxy and piperazine as amine, at a mass ratio of 9: 1) onto the fiber surface, which remarkably enhanced the interfacial adhesion.^{22–24} Tian and coworkers introduced the epoxy group onto the aramid fiber surface by

the self-polymerization of dopamine, followed by grafting epoxy functionalized silane.²⁷ Due to the strong interaction between epoxy groups and the rubber matrix, the single-fiber pull-out tests showed that the interfacial adhesion increased by 62.5%.

Synthesis of PPTA with various substituents through homopolymerization or copolymerization represents another effective approach to improve its compatability with other polymers.^{28–34} For example, the hydroxy group was known to improve the affinity of PPTA toward epoxy,³² while the propargyl group enhanced interfacial adhesion toward rubber.³¹ However, in most cases, one type of functional groups is only effective to one type of polymer matrices. It occurred to us if both unsaturated group and polar group be introduced on the phenyl ring of PPTA, the resultant polymer could be used alone or as a sizing agent to improve interfacial adhesion toward either epoxy resin or rubber matrix.

Claisen rearrangement reaction (CR) is a classic organic reaction in which allyl vinyl ether isomerizes to the molecule bearing two functional groups³⁵ and offered a powerful tool for organic synthesis.^{36–39} Much work has been carried out in small molecules but rare in macromolecules. In our previous short communication,⁴⁰ we reported a facile and efficient method to obtain a novel PPTA bearing both apolar allyl and polar hydroxy groups on each terephthaloyl unit by a combination of the step-growth polymerization and subsequent thermally induced CR. The resultant polymer was used as a sizing agent to improve the interfacial property of Kevlar fiber-rubber composite. Under identical and un-optimized conditions, the fibers treated with as low as 0.1 and 0.5 wt % polymer solution in NMP displayed pullout force of 25.0 and 30.1 N, respectively, which were obviously larger than that of the fiber without treatment (20.8 N). It was rationalized by the good compatability of the polymer to the fiber and the high reactivity of unsaturated allyl group toward vulcanization.

In the present work, we extend the scope of this strategy to Kevlar fiber-epoxy composites. To optimize the polymer structure, eight (co)polyamides, poly(*p*-phenylene terephthalamide)-*ran*-poly[*p*-phenylene 2,5-bis(allyloxy)terephthalamide], were prepared via low temperature solution copolycondensation of *p*-phenylene diamine, terephthaloyl chloride, and 2,5-bis(allyloxy)terephthaloyl chloride. They were abbreviated as APPTA-*x*, where *x* (=0, 5, 25, 50, 60, 75, 90, and 100) represents the molar fraction of allyloxy substituted structure unit. Except for APPTA-0 and 100, all others are new polymers. These polymers were subjected to CR at 190 °C in NMP and converted to the corresponding products, CRPPTA-*x*, that bear various content of hydroxy and allyl groups. All the rearranged polymers showed improved solubility and those with high co-unit contents, that is, CRPPTA-60, 75, 90, and 100, were readily dissolved in *m*-cresol, DMF, DMAc, DMSO, and NMP. The effects of these four polymers, as sizing agents, on the interfacial adhesion between Kevlar fiber and epoxy resin were estimated by contact angle

method, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and microbond tests. The copolymer composition and concentration were found to play an important role in influencing interfacial structure and property.

EXPERIMENTAL

Materials

The aramid fibers with a diameter of 15 μm were kindly supplied by He Bei Silicon Valley Corporation and were extracted with acetone for 24 h before use. E-51 epoxy resin and hardener were purchased from Tianjin Woosin Co. at a resin to hardener ratio of 2:1. 1-Bromobutane (Chemical pure, Sinopharm Chemical Reagent) was purified by atmospheric distillation. *m*-Cresol was purified by reduced pressure distillation. Dimethyl sulfoxide (DMSO, AR, Beijing Chemical Co.) and N-methyl-2-pyrrolidone (NMP, AR, Beijing Chemical Co.) were dried over CaH₂, distilled under reduced pressure and stored over dry molecular sieves. *p*-Phenylenediamine (AR, J&K) was sublimated twice under vacuum before use. Calcium chloride (AR, Beijing Chemical Co.) was finely ground and dried at 400 °C in muffle furnace for 4 h to remove residue water. Pyridine (AR, Beijing Chemical Co.) was dried over KOH pellets and distilled out before use. 2,5-Bis(allyloxy)terephthaloyl chloride and *N,N'*-diphenyl 2,5-bis(allyloxy)terephthalamide were prepared according to the previously reported procedure.⁴⁰ All other reagents and solvents were used as received unless otherwise specified.

Synthesis of Copolymers

Allyloxy Substituted Copolymers (APPTA-*x*)

The preparation of APPTA-75 is described as an example to describe polymerization procedure. Into a four-neck round bottom flask, 8.22 g of CaCl₂ and 100 mL of dry NMP were introduced under N₂ atmosphere. The mixture was heated until all the salts totally dissolved. To the resultant solution, 3.60 g (33.3 mmol, 1 equiv.) of *p*-phenylenediamine was added. To the obtained mixture cooled to −10 °C, 7.87 g (25.0 mmol, 0.75 equiv.) of 2,5-bis(allyloxy)terephthaloyl chloride and 1.69 g (8.0 mmol, 0.25 equiv.) of terephthaloyl chloride were added with gentle stirring. When the mixture became well distributed, 4.70 g (59.4 mmol, 1.8 equiv.) of pyridine was injected and the stirring speed was increased. After the reaction continued for 20 min in cool bath, the temperature was raised to room temperature. The reaction mixture solidified gradually and the stirring was continued until the apparent viscosity did not rise. The reaction mixture was poured into large amount of distilled water. The solids were collected by filtration, followed by washing with boiling water, ethanol and acetone. After drying at 80 °C for 24 h under vacuum, 9.50 g of yellow powders were obtained. Yield: 89%.

N-Butylated Allyloxy Substituted copolymers

Into a schlenk tube containing 60 mg of NaH (2.5 mmol, 1 equiv., 60% suspension in paraffin), 25 mL of DMSO was added in N₂ atmosphere.⁴¹ The mixture was kept at 70 °C

for 1 h and then cooled to 30 °C. Afterward, 0.40 g (2.5 mmol amide unit) of APPTA-75 was added. The reaction mixture became red and the viscosity gradually rose. When a clear solution was obtained, 0.68 g (5.0 mmol, 2 equiv.) of 1-bromobutane was injected and the reaction was allowed to continue for 18 h. The reaction mixture was poured into 500 mL of distilled water and extracted with 3×150 mL portions of dichloromethane. The organic layers were combined and washed with brine and dried with anhydrous Na_2SO_4 . The solution was evaporated with a rotary evaporator to 10 mL and added slowly to 150 mL of petroleum ether. The precipitates were collected by filtration. After drying under vacuum, 0.38 g of white powders (referred as N-B-APPTA-75) were obtained. Yield: 70%. Other *N*-butylated products were prepared using the similar method and referred as N-B-PPTA, N-B-APPTA-5, N-B-APPTA-25, N-B-APPTA-50, N-B-APPTA-60, N-B-APPTA-90, and N-B-APPTA-100, respectively.

***N,N'*-Dibutyl-*N,N'*-Diphenyl 2,5-Bis(Allyloxy) Terephthalamide**

This compound was synthesized with a method similar to N-B-APPTA-75. ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.20–7.00 (m, 6 H, Ar), 6.98–6.60 (m, 4 H, Ar), 6.53–6.37 (s, 2H, Ar), 6.08–5.80 (m, 2 H, vinyl), 5.46–5.15 (t, 4 H, vinyl), 4.52–4.14 (d, 4 H, CH_2), 3.99–3.71 (t, 4 H, CH_2), 1.69–1.45 (m, 4 H, CH_2), 1.45–1.15 (m, 4 H, CH_2), 1.00–0.80 (t, 6 H, CH_3). ^{13}C NMR (400 MHz, CDCl_3 , δ , ppm): 167.71, 147.72, 142.03, 133.18, 128.49, 128.39, 127.65, 126.89, 117.06, 113.07, 69.59, 49.02, 29.81, 20.03, 13.83. HRMS (ESI, m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{O}_4$, 541.3066; found, 541.3059. Anal. calcd. for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{O}_4$: C, 75.53; H, 7.46; N, 5.18; Found: C, 75.60; H, 7.40; N, 5.18.

Claisen Rearrangement Reaction of Copolymers and Sizing of Fibers

Take APPTA-75 as an example. Into a reaction tube were introduced 100 mg of (0.47 mmol allyloxy containing unit) APPTA-75, 50 mg (0.47 mmol) of *m*-cresol and 2 mL of NMP. After three freeze–pump–thaw cycles, the tube was sealed under vacuum and heated at 190 °C for 6 h. The tube was broken and the clear solution was diluted with 6 mL of NMP and dropped into 150 mL of methanol. The precipitates were collected by filtration, followed by washing with methanol and drying under vacuum at ambient temperature for 24 h. The resulted yellow solids (referred as CRPPTA-75) weighed 70 mg. Yield: 70%.

The sizing solutions were prepared following a similar procedure except for polymer concentration. The extracted aramid fibers were immersed in the sizing solution and stood for 10 min, and dried in vacuum at 70 °C for 3 h. The sized fibers were referred as AF-CRPPTA-*x*-*y*, where AF and *y* indicated the aramid fibers extracted with acetone and the weight percentage concentration of CRPPTA-*x* of sizing solution, respectively.

Sample Preparation for Microbond Test

Microbond test was carried out to estimate the interfacial property between fibers and epoxy resins. The aramid monofilament was fixed on a paper frame with a dimension of 26 mm \times 58 mm. The epoxy resin droplet with desired size was placed on the monofilament and cured at 40 °C for 2 h, 80 °C for 2 h, and 120 °C for 0.5 h.

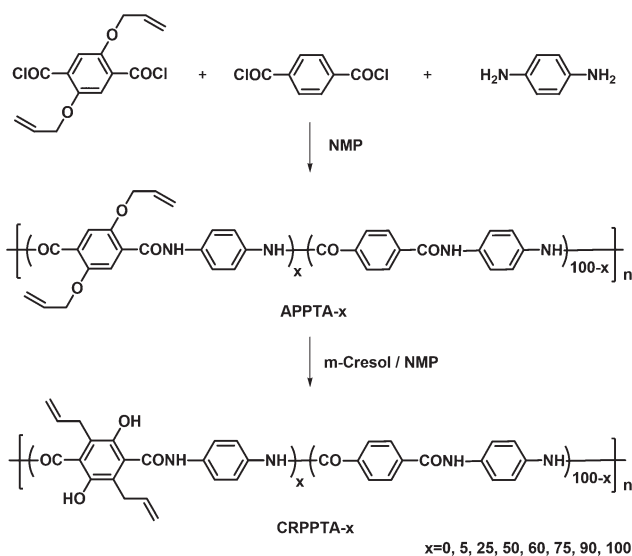
Characterization

Solid state ^{13}C NMR experiments were performed on a Bruker 400 MHz WB Solid-State NMR Spectrometer (AVANCE III). ^1H NMR spectra were recorded on a Bruker ARX 400 MHz NMR spectrometer with CDCl_3 or d_6 -DMSO as the solvent and tetramethylsilane as the internal reference. Thermogravimetric analyses (TGA) were run on a TA SDT 2960 instrument. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) s were obtained with a TA DSC Q100 instrument at a heating rate of 5 °C/min under nitrogen atmosphere. The number-average molecular mass (M_n), weight-average molecular mass (M_w), and molecular mass polydispersity (M_w/M_n) were estimated by gel permeation chromatography (GPC) equipped with a Waters 2410 refractive index detector and a Waters 515 pump. THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. The GPC curves were calibrated against a series of monodispersed polystyrene standards. One-dimensional powder wide-angle X-ray diffraction experiments were carried out on a Philips X'Pert Pro instrument with a 3000 W ceramic tube as the X-ray source ($\text{CuK}\alpha$) and an X'celerator detector. The surface chemical compositions of aramid fibers were estimated by X-ray photoelectron spectroscopy (XPS) using a Axis Ultra instrument (Kratos Analytical, England) with a monochromatic Al K α source (1486.7 eV photons) running at a power of 225 W. All binding energies were using C1s hydrocarbon peak at 284.8 eV as the reference. CasaXPS was used to analyze the data. The contact angle and surface energy of the fibers were determined according to Yao's work,⁴² and *n*-octane and glycerol were used as probe liquids, respectively. A microbond testing was carried out to determine the interfacial shear strength (IFSS) of the Kevlar fiber/epoxy resin composite using an interfacial micro-bond evaluation instrument (Model HM410) made by Tohei Sanyon Corporation of Japan. The surface morphologies of CFs and debonded CFs were observed by a scanning electron microscopy (FE-SEM S-4800, Hitachi, Japan).

RESULTS AND DISCUSSION

Synthesis of Allyloxy Substituted PPTA

The copolymers APPTA-*x* were synthesized via low temperature solution copolycondensation of 2,5-bis(allyloxy)terephthaloyl chloride, terephthaloyl chloride and *p*-phenylenediamine at various feed ratios in NMP containing 8 wt % CaCl_2 (Scheme 1). In total, eight samples were obtained. All of them had good thermal stabilities and the temperature of 5% weight loss under nitrogen atmosphere were higher than 350 °C (Table 1). Since apolar allyloxy



SCHEME 1 Synthesis and Claisen rearrangement reaction of APPTA-*x* copolymers.

substituents and polymer main-chain have distinct requirements for solvent, all the copolymers including APPTA-100 were not soluble in all the solvents tested. Solid state ^{13}C NMR spectroscopy was first employed to characterize the structures of APPTA-*x*. As shown in Figure 1, the carbonyl carbon atoms of PPTA showed a resonance absorption at 162 ppm, while the aromatic carbon atoms were located in the range of 112–138 ppm.⁴⁰ The incorporation of allyloxy groups on the terephthaloyl unit yielded new absorptions at 157 and 60 ppm, which were attributed to the substituted carbon atom **d** of phenyl ring and methylenic carbon atom **e** of allyloxy, respectively. In addition, other signals shifted upfield due to the electron donating nature of the allyloxy substituent. These variations became more remarkable as the content of allyloxy substituted unit increased.

The chemical structure of APPTA-*x* was further characterized by FT-IR (Fig. 2). The absorptions of N-H stretching, amide I and II of PPTA were presented at 3324, 1650, and

TABLE 1 Properties of APPTA-*x* Copolymers

Sample	η_{inh}^a	T_d (°C) ^b	$M_n \times 10^{-3c}$	PDI ^c
PPTA	7.49	525	37.0	2.02
APPTA-5	–	509	23.0	1.91
APPTA-25	–	417	22.0	1.88
APPTA-50	–	388	31.0	1.98
APPTA-60	–	367	21.0	2.09
APPTA-75	–	359	11.0	2.25
APPTA-90	–	351	10.0	2.12
APPTA-100	–	357	9.6	1.99

^a Measured in 98% H_2SO_4 at 30 ± 0.1 °C ($c = 0.5$ g/dL).

^b 5% weight loss temperature. Heating rate, 10 °C/min; atmosphere, N_2 .

^c Butyl substituted samples estimated by GPC with a calibration against polystyrene standards.

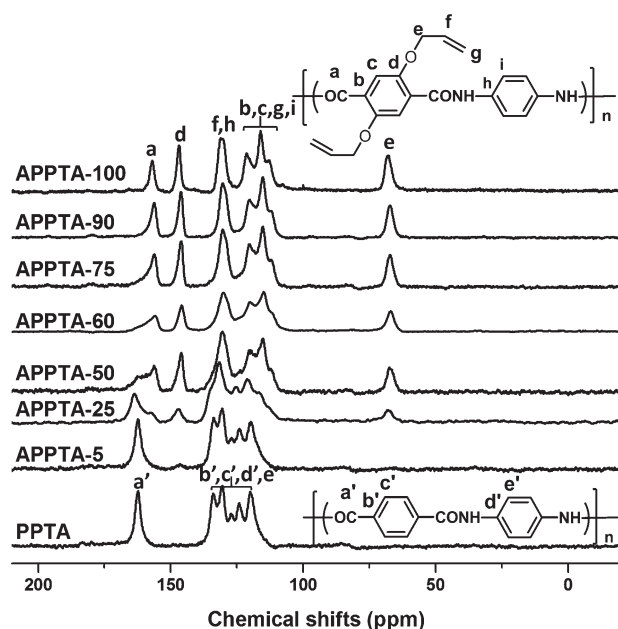


FIGURE 1 Solid state ^{13}C NMR spectra of APPTA-*x* copolymers.

1541 cm^{-1} , respectively. With an increase of the co-unit content, the unsymmetric and symmetric stretching absorptions of C-O-C of phenyl allyl ether appeared at 1193 and 1000 cm^{-1} , and became stronger. Moreover, the amide absorptions blue-shifted, an indicative of the disruption of intermolecular hydrogen bonding. This was consistent with 1D WAXD results, which will be discussed below.

It was evident from Figure 3 that PPTA exhibited two diffraction peaks attributed to (110) and (200) planes.⁴³ APPTA-5 showed almost identical diffraction pattern to PPTA, implying no discernible effect of allyloxy substitution on the intermolecular packing. As the content of co-unit increased, these two peaks became diffused and disappeared gradually, and two new sharp diffraction peaks centered at 9.2 and 26.3°,

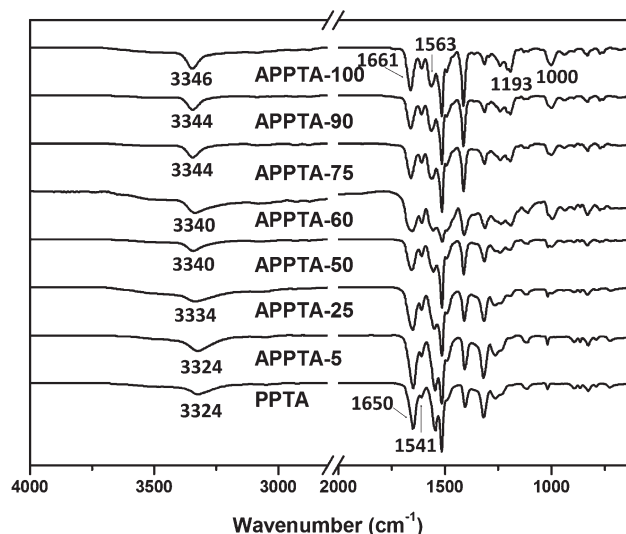


FIGURE 2 FT-IR spectra of APPTA-*x* copolymers.

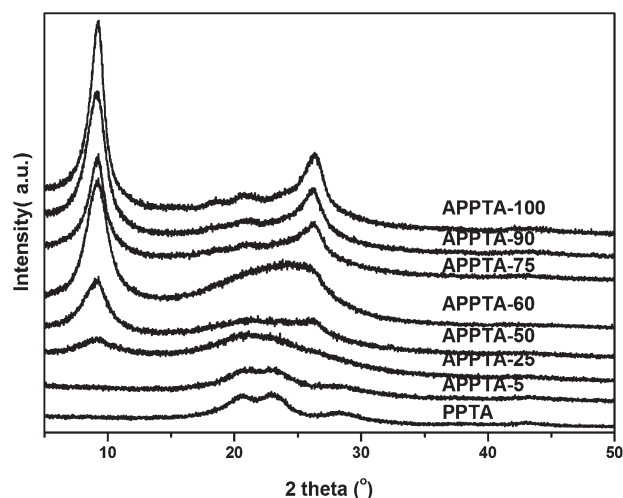
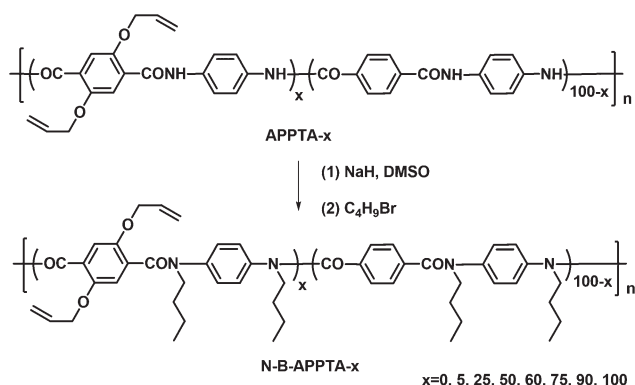


FIGURE 3 1D WAXD patterns of APPTA-x copolymers.

respectively, were observed, suggesting that a more ordered crystalline structure, distinct to that of PPTA was formed.

To shed light on the molar mass of APPTA-x, the amide groups were substituted by *n*-butyl groups according to Takayanagi's method (Scheme 2).³⁵ The resultant polymers, abbreviated as N-B-APPTA-x, are readily dissolved in THF and chloroform due to the absence of intermolecular hydrogen bonding. Figure 4 displayed the ¹H NMR spectra of these polymers. The butyl substituent showed resonance peaks at 3.78, 1.48, 1.30, and 0.87 ppm, respectively. The broad resonance peaks at 5.79, 5.11, and 4.48 ppm were attributed to the protons of $-O-CH_2-CH=CH_2$, $-O-CH_2-CH=CH_2$, and $-O-CH_2-CH=CH_2$, respectively. The broadening of allyloxy groups were probably due to the steric hindrance caused by N-butylation, which could hinder the rotation around amide linkage.^{44,45} To prove this speculation further, the model compound *N,N'*-dibutyl-*N,N'*-diphenyl 2,5-bis(allyloxy)terephthalamide (N-B-CM) was prepared (Scheme 3). It was fully characterized by ¹H/¹³C NMR (Supporting Information Figs. S1 and S2), mass spectroscopy and elementary analysis. Figure 5 shows the temperature variable ¹H NMR spectra of this compound. The assignment of each proton was made by 2D-NOESY spectrum (Supporting Information Fig. S1). At 50



SCHEME 2 N-Butylation of APPTA-x copolymers.

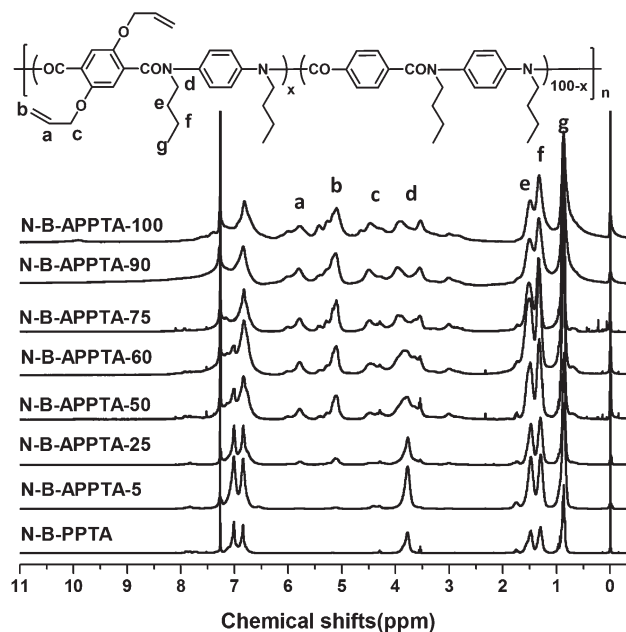


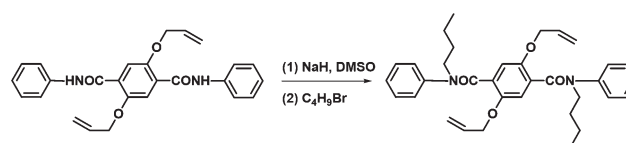
FIGURE 4 ¹H NMR spectra of N-B-APPTA-x copolymers in CDCl₃ at room temperature.

°C, all the protons exhibit well resolved absorption peaks. However, at lower temperatures, these peaks become relatively weak and diffusion. The ¹H NMR spectra of N-butylation copolymers show no such temperature dependence due to the restricted chain mobility (Supporting Information Fig. S3).

Based on the area ratio of allyloxy to the butyl protons, it could be concluded that all the amide groups were substituted. The molecular weights of the N-butylation polymers were evaluated by GPC (Table 1). For PPTA with an inherent viscosity of 7.49 dL/g, a number-averaged molecular mass of 37,000 g/mol was estimated, which was comparable to the results obtained by Ying et al.⁴⁶ and Mourey et al.⁴⁷

CR Reaction of APPTA-x

CR reactions of APPTA-x were carried out in NMP at 190 °C for 6 h. At the beginning, APPTA-x was suspended in NMP. As the reaction proceeded, the suspensions of APPTA-60, 75, 90, and 100 became clear solution gradually, while the others remained heterogeneous. After the reaction was completed, the solution was dropped into methanol slowly and the rearranged product CRPPTA-x was obtained.⁴⁸ The solubility of CRPPTA-x was much better than APPTA-x (Table 2). Although the copolymers containing co-units less than 60 mol %, that is, CRPPTA-5, 25, and 50, were just partially soluble in NMP, DMSO, DMAc, DMF, and m-cresol, 2 mg of



SCHEME 3 Synthesis of model compound N-B-CM.

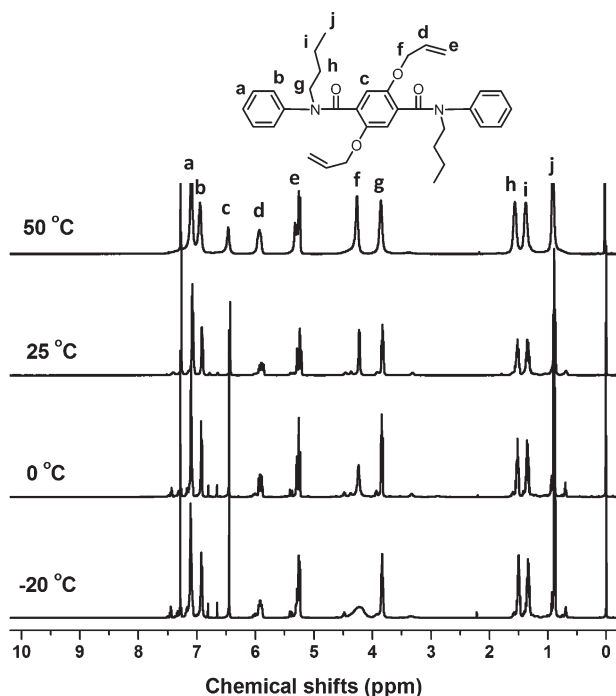


FIGURE 5 Temperature variable ^1H NMR spectra of N-B-CM recorded in CDCl_3 .

other copolymers were completely dissolved in 1 mL of those solvents at room temperature. Taking the advantage of good solubility, CRPPTA-60, 75, 90, and 100 were characterized by ^1H NMR (Fig. 6). The resonance peak of proton **a** at 10.36 ppm attributed to amide protons in PPTA part and the peak **d** at 8.12 ppm attributed to the phenyl protons adjacent to $-\text{C}=\text{O}$ group became weaker from APPTA-60 to APPTA-100 and the peak **c** attributed to $-\text{OH}$ proton and other peaks became stronger relatively. Above results suggest that APPTA-*x* copolymer underwent CR reaction. The occurrence of CR reaction was also confirmed by DSC in solid state as shown in Supporting Information Figure S4. The increase of solubility was probably for that the introduction of hydroxy group enhanced the interaction between the polymer with the solvent and destroyed the dense packing of PPTA main chains.

The CRPPTA-*x* was also characterized by FT-IR. As shown in Figure 7, from CRPPTA-60 to CRPPTA-100, the resonance

peak near 3310 cm^{-1} became broader, and a new peak appeared at higher wavenumber; this was because more hydroxy group formed in the polymer and the peak attributed to the hydroxy group became more obvious. As shown in Figure 8, all the polymers showed two broad diffraction peaks at 9.2° and 21.0° , greatly different from that of APPTA-*x*, which suggested that these polymers formed amorphous structure.

Surface Chemical Compositions of Sized Fibers

One potential application of CRPPTA-*x* is to enhance the interfacial adhesion between aramid fibers and the matrices of composites, as a reinforcing material alone or a sizing agent. CRPPTA-100 has been known to improve the interface property of Kevlar/rubber composite.⁴⁰ To demonstrate the effect of the target polymer on the interfacial structure and property of aramid fiber/epoxy composite, aramid fibers were dipped into 0.5 wt % solution of CRPPTA-60, 75, 90, and 100 in NMP for 10 min, respectively. After complete drying under vacuum, the surface chemical compositions of the treated fibers were ascertained by XPS. All the fibers showed the characteristic peaks of C1s, N1s, and O1s (Supporting Information Fig. S5). The C1s core level spectrum was curve-fitted into five peaks, at 284.8 eV for C-C species, 285.8 eV for C-N species, 286.5 eV for C-O species, 287.9 eV for C=O species, and 289.1 eV for O=C-O species. The carbon, nitrogen, and oxygen concentrations of the fiber surface were summarized in Table 3. Compared with the unsized fibers, an increase of O/C ratio from 0.14 to 0.19 was achieved, implying the sizing agents were introduced onto the fiber surface successfully. The slight modification in O/C ratio was reasonable considering the similar chemical structures of aramid fibers and sizing agent.

Surface Free Energy of Sized Fibers

The surface free energy of sized fibers was estimated by the contact angle method using *n*-octane and glycerol as probe liquids, respectively. The results were listed in Table 4. The contact angle of *n*-octane on the sized fiber didn't vary significantly with the copolymer composition. However, that of glycerol decreased obviously with an increase of co-unit contents due to the incorporation of polar hydroxy group. The naked fibers showed a surface free energy of 35.9 mJ/m^2 , whereas the fibers sized with CRPPTA-100 exhibited a value

TABLE 2 Comparison of Solubility of APPTA-*x* With CRPPTA-*x* in Common Solvents^a

Sample	PPTA	APPTA-5 (CRPPTA-5)	APPTA-25 (CRPPTA-25)	APPTA-50 (CRPPTA-50)	APPTA-60 (CRPPTA-60)	APPTA-75 (CRPPTA-75)	APPTA-90 (CRPPTA-90)	APPTA-100 (CRPPTA-100)
NMP	—	— (—)	+— (—)	+— (+—)	+— (++)	+— (++)	— (++)	— (++)
DMSO	—	— (—)	— (—)	+— (+—)	+— (++)	+— (++)	+— (++)	— (++)
<i>m</i> -Cresol	—	— (—)	— (—)	— (+—)	+— (+—)	+— (+—)	+— (+—)	+— (++)
NMP + 5%LiCl	—	+— (+—)	+— (—)	+— (+)	+— (++)	+— (++)	+— (++)	+— (++)
DMAc + 5%LiCl	—	+— (+—)	+— (+—)	+— (+—)	+— (++)	+— (++)	— (++)	— (++)
DMF + 5%LiCl	—	— (—)	— (—)	— (+—)	+— (++)	— (++)	— (++)	— (++)

^a For 2 mg polymer in 1 mL solvent; ++: soluble at 25°C ; +: soluble at 60°C ; +—: partly soluble at 60°C ; —: insoluble.

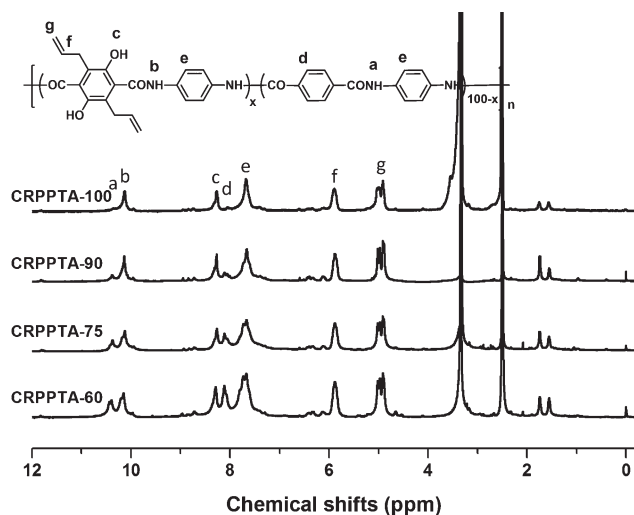


FIGURE 6 Comparison of ^1H NMR spectra of CRPPTA- x copolymers in d_6 -DMSO at room temperature.

of 43.2 mJ/m^2 . The increased surface free energy implied that the fibers were more easily wetted by polar liquids such as epoxy resin and therefore facilitate the preparation of high performance composites.

Interfacial Adhesion of Aramid Fiber/Epoxy Composites

The interfacial adhesions between aramid fibers and epoxy resins were evaluated by microbond tests and the IFSS were listed in Table 5. The IFSS of fibers with various weight concentrations of CRPPTA-60 were first compared. As shown in Figure 9, the IFSS of naked fibers was 37.8 MPa . The treatment with $0.05 \text{ wt } \%$ CRPPTA-60 increased IFSS of the fibers to around 40 MPa . Further increase in IFSS could be obtained by increasing the polymer concentration till $0.5 \text{ wt } \%$. Beyond that point, the IFSS dropped dramatically to 33.9 MPa for AF-CRPPTA-60-1 and 31.8 MPa for AF-CRPPTA60-2. $0.5 \text{ wt } \%$ was an optimal concentration for CRPPTA-60 to

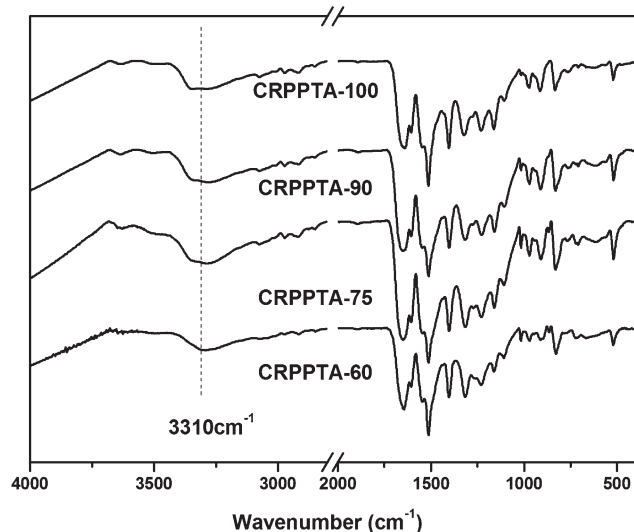


FIGURE 7 Comparison of FT-IR spectra of CRPPTA- x copolymers.

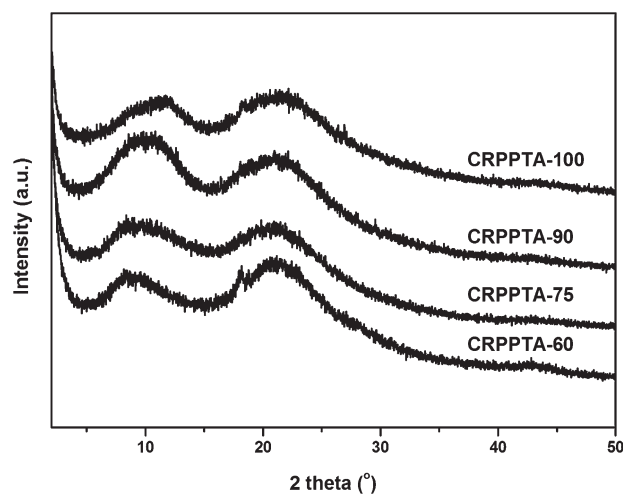


FIGURE 8 1D WAXD patterns of CRPPTA- x copolymers.

TABLE 3 XPS Elementary Analysis of Aramid Fibers

Sample	Atom %				Atom ratio
	C	O	N	Ca	O/C
AF	82.54	11.64	4.71	1.12	0.14
AF-CRPPTA-60-0.5	82.96	11.95	4.24	0.86	0.14
AF-CRPPTA-75-0.5	81.56	12.90	4.31	1.23	0.16
AF-CRPPTA-90-0.5	81.87	13.05	4.16	0.92	0.16
AF-CRPPTA-100-0.5	80.60	14.99	3.36	1.05	0.19

size the chosen aramid fibers. It might be inferred that low concentration sizing would cause little effect on the surface property of fibers while too much sizing would cause defec-tions on the surfaces of the fibers due to the agglomeration of sizing agent molecules.

The IFSSs of Kevlar fibers sized with other copolymers were also measured (Fig. 10). The copolymer CRPPTA-60 with $60 \text{ mol } \%$ substituted co-units displayed the best performance. It is probably due to its high affinity toward both fibers and epoxy resins and also its relatively high molecular weight.

TABLE 4 The contact angle of fibers with n -octane and glycerol and the calculated surface free energy

Sample	Contact angle				
	With octane (Θ_1)	With glycerol (Θ_2)	γ_s^d (mJ/m 2)	γ_s^p (mJ/m 2)	γ_s (mJ/m 2)
AF	45.3 ± 1.9	60.7 ± 1.3	15.8	20.1	35.9
AF-CRPPTA-60-1	46.6 ± 1.8	54.4 ± 1.5	15.5	26.0	41.5
AF-CRPPTA-75-1	46.4 ± 2.0	53.0 ± 1.3	15.6	27.2	42.8
AF-CRPPTA-90-1	47.5 ± 1.8	53.9 ± 1.7	15.3	26.8	42.1
AF-CRPPTA-100-1	47.0 ± 1.4	52.6 ± 1.9	15.4	27.8	43.2

TABLE 5 Interfacial Shear Strength (IFSS) of Different Fibers With Epoxy Resin

Sample	IFSS (MPa)
AF	37.8 ± 2.9
AF-CRPPTA-60-0.05	40.7 ± 3.0
AF-CRPPTA-60-0.1	44.3 ± 2.9
AF-CRPPTA-60-0.2	42.7 ± 2.7
AF-CRPPTA-60-0.5	44.9 ± 3.0
AF-CRPPTA-60-1	33.9 ± 2.9
AF-CRPPTA-60-2	31.8 ± 3.0
AF-CRPPTA-75-0.5	37.5 ± 2.6
AF-CRPPTA-90-0.5	39.5 ± 2.9
AF-CRPPTA-100-0.5	36.0 ± 2.9

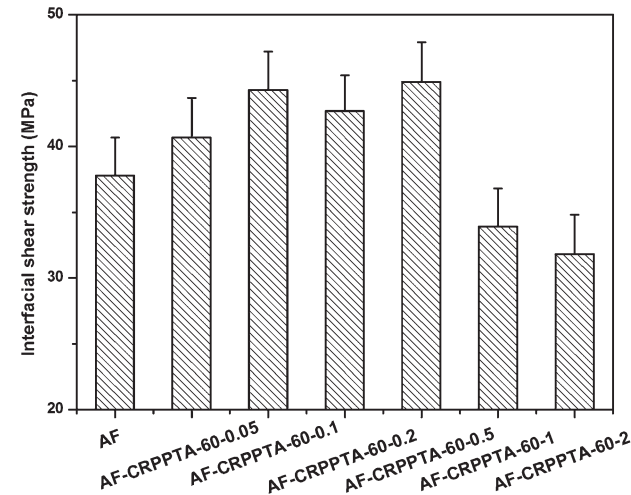


FIGURE 9 Interfacial shear strength (IFSS) of epoxy resin and the aramid fibers sized by CRPPTA-60 at various concentrations.

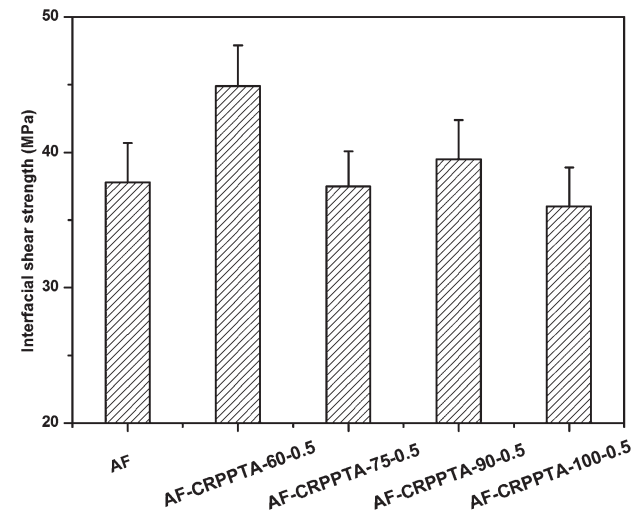


FIGURE 10 Interfacial shear strength (IFSS) of epoxy resin and the aramid fibers sized by different polymers at a concentration of 0.5 wt %.

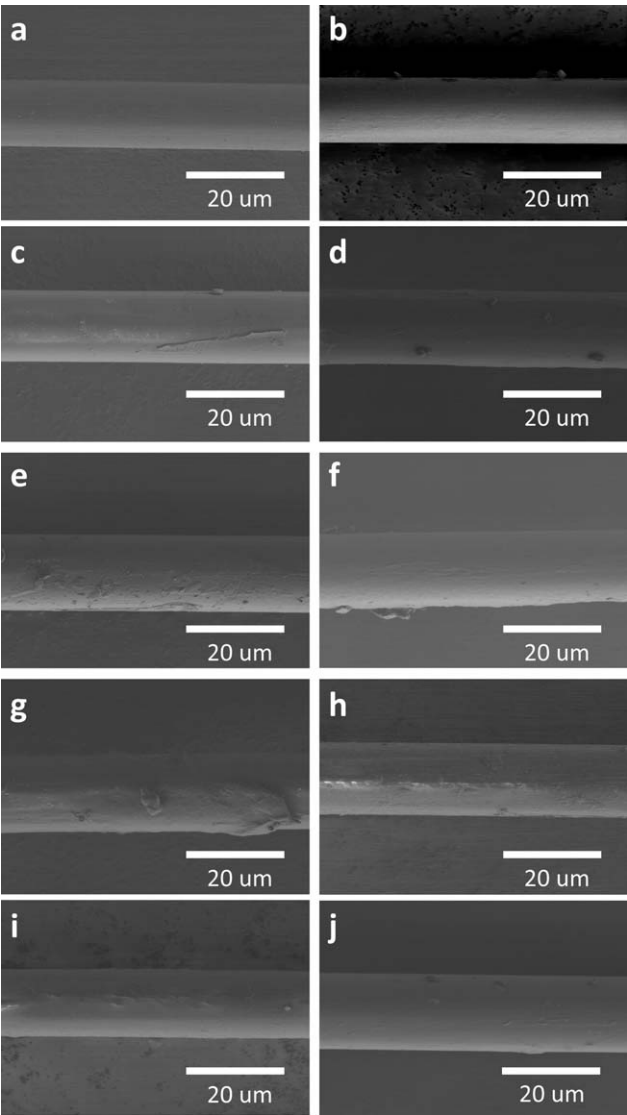


FIGURE 11 Surface SEM images of naked aramid fibers AF (a) and the sized ones: (b) AF-CRPPTA-60-0.05, (c) AF-CRPPTA-60-0.1, (d) AF-CRPPTA-60-0.2, (e) AF-CRPPTA-60-0.5, (f) AF-CRPPTA-60-1, (g) AF-CRPPTA-60-2, (h) AF-CRPPTA-75-0.5, (i) AF-CRPPTA-90-0.5, and (j) AF-CRPPTA-100-0.5.

Surface Morphology of Sized Fibers

The surface morphologies of the aramid fibers before and after sizing with CRPPTA were characterized by SEM, as shown in Figure 10. The extracted fibers showed very clean and smooth surfaces [Fig. 11(a)]. With an increase of polymer concentration, the coating of surface became evident [Fig. 11(b–e)]. For AF-CRPPTA-60-1 and AF-CRPPTA-60-2, the surface became quite rough and there were even agglomeration on their surfaces [Fig. 11(f,g)]. The surface morphologies of AF-CRPPTA-75-0.5, AF-CRPPTA-90-0.5, and AF-CRPPTA-100-0.5 showed no discernible difference from that of AF-CRPPTA-60-0.5 [Fig. 11(h,i,j)]. These results were in consistence with that of XPS, both indicating the uniform sizing layer were formed on the aramid surface.

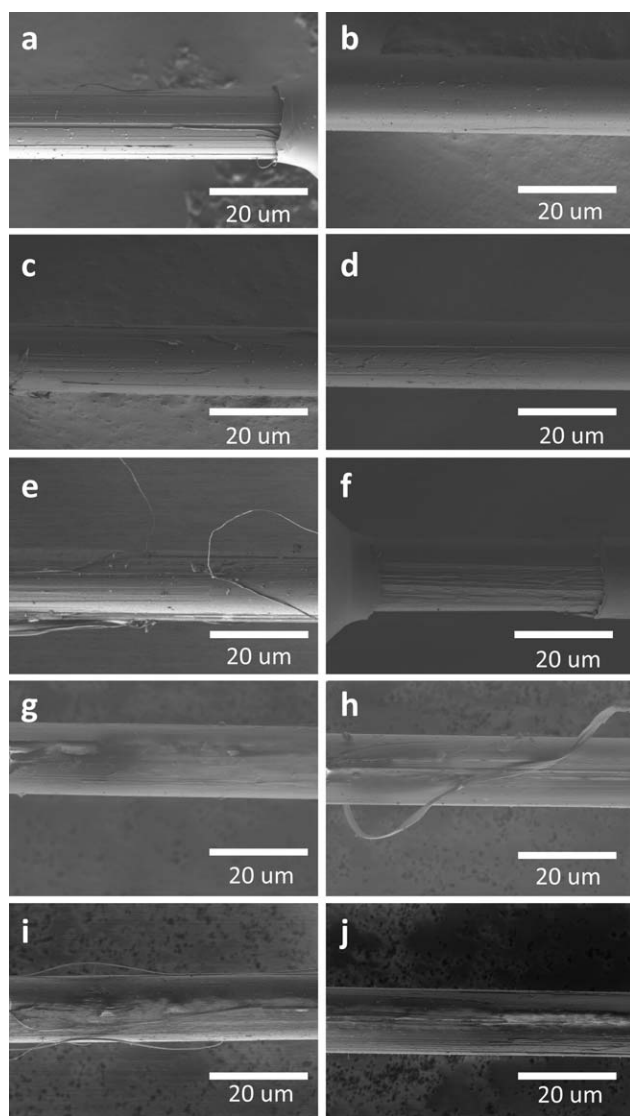


FIGURE 12 Fractured surface SEM images of naked aramid fibers AF (a) and the sized ones: (b) AF-CRPPTA-60-0.05, (c) AF-CRPPTA-60-0.1, (d) AF-CRPPTA-60-0.2, (e) AF-CRPPTA-60-0.5, (f) AF-CRPPTA-60-1, (g) AF-CRPPTA-60-2, (h) AF-CRPPTA-75-0.5, (i) AF-CRPPTA-90-0.5, and (j) AF-CRPPTA-100-0.5.

The morphology of the fractured surface is helpful to understand the interfacial adhesion mechanism between fiber and matrix. For AF/epoxy resin composite, the fracture surface was quite smooth and little epoxy were adhered [Fig. 12(a)]. For the epoxy-based composites reinforced by AF-CRPPTA-60-0.05, AF-CRPPTA-60-0.1, AF-CRPPTA-60-0.2, and AF-CRPPTA-60-0.5, respectively, the fractured surfaces became more and more rough [Fig. 12(b-e)]. For those sized by AF-CRPPTA-60-0.5, some resins were adhered on the fiber surface. Further increasing the polymer concentration as in AF-CRPPTA-60-1 and AF-CRPPTA-60-2 led to even rougher fiber surface [Fig. 12(f,g)]. It seemed that there was little epoxy resin remained on the surface of the fibers sized by AF-CRPPTA-75-0.5, AF-CRPPTA-90-0.5, and AF-CRPPTA-100-0.5

[Fig. 12(h,i,j)]. Based on these results, it could be inferred that the failure occurred at the sizing agent/fiber interface.

CONCLUSIONS

A series of polar hydroxy and unsaturated allyl substituents containing aromatic copolyamides, CRPPTA-x, were prepared through low temperature solution polycondensation of *p*-phenylenediamine, terephthaloyl chloride, and 2,5-bis(allyloxy)terephthaloyl chloride, followed by Claisen rearrangement reaction. The copolymers with high co-unit contents, that is, CRPPTA-60, 75, 90, and 100, exhibited much improved solubility in NMP, DMF, DMAc, DMSO, and *m*-cresol. The solutions of these four copolymers in NMP, as sizing agents, increased the surface energy, O/C ratio and roughness of aramid fibers. The copolymer composition and concentration had remarkable effects on the interfacial structure and property of epoxy-based composites. For CRPPTA-60, the IFSS of the sized fibers increased with an increase of copolymer concentration and reached a maximum at 0.5 wt %, which showed a 19% increase of IFSS compared with the unsized AF/epoxy resin composites. Increasing the content of co-unit in the copolymer lead to a poorer IFSS. This might be attributed to the reduced chemical affinity of copolymer toward the fiber surface. The fractured surface morphological studies suggested that the failure probably lay at the sizing agent/aramid fiber interface. This work showed great potential for enhancement of interfacial adhesion between aramid surface/matrix with a simple procedure for industrial use and being universal for different matrix.

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